



Detection of hydrogen peroxide produced at a liquid/liquid interface using scanning electrochemical microscopy

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ABSTRACT

Scanning electrochemical microscopy (SECM) was used to monitor *in situ* hydrogen peroxide (H_2O_2) produced at a polarized water/1,2-dichloroethane (DCE) interface. The water/DCE interface was formed between a DCE droplet containing decamethylferrocene (DMFc) supported on a solid electrode and an acidic aqueous solution. H_2O_2 was generated by reducing oxygen with DMFc at the water/DCE interface, and was detected with a SECM tip positioned in the vicinity of the interface using a substrate generation/tip collection mode. This work shows unambiguously how the H_2O_2 generation depends on the polarization of the liquid/liquid interface, and how proton-coupled electron transfer reactions can be controlled at liquid/liquid interfaces.

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1. Introduction

The interface between two immiscible electrolyte solutions (ITIES), is well-suited to carry out proton-coupled electron transfer reactions [1–3], i.e., protons can be provided from the aqueous side, and lipophilic electron donors or acceptors can be located in the organic side. Furthermore, by controlling the polarization of the interface, it is possible to control the rate of either proton or electron transfer across the interface. Recently, we have investigated oxygen reduction by lipophilic donors in 1,2-dichloroethane (DCE) in contact with aqueous acid solutions and shown that the final product of this biphasic reaction was hydrogen peroxide (H_2O_2) in water [4].

Herein, scanning electrochemical microscopy (SECM) was employed for the detection of H_2O_2 generated at a water/DCE interface. SECM is a well-established technique with a key advantage of localizing and detecting interfacial electrochemical reactions [5] and has been widely employed to detect H_2O_2 produced by the oxygen reduction reaction (ORR) on various solid substrates [6–8]. In this work, the water/DCE interface was formed between a DCE droplet containing DMFc supported on a solid electrode and immersed in an acidic aqueous solution. The SECM tip was positioned close to the water/DCE droplet interface in the top aqueous solution. With this configuration, the polarization of the water/DCE interface to drive the proton transfer to allow oxygen

reduction with DMFc on the organic side of the interface was found to be concomitant with the amperometric detection H_2O_2 by the SECM tip biased at a potential for the oxidation of H_2O_2 . The different SECM parameters, including the tip-interface distance and interfacial Galvani potential difference, have been optimized for an efficient H_2O_2 detection.

2. Experimental

All chemicals were used as received. The organic supporting electrolyte was bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate (BTTPATPFB) [9]. All aqueous solutions were prepared with Milli-Q reagent water (Millipore, > 18.2 M Ω /cm) and the DCE (Synthesis Grade, SDS) was saturated with water prior to use.

All the electrochemical measurements were carried out on a CHI 900 SECM (CH Instruments, Austin, TX) at room temperature with air-saturated solutions. A 5 μ L DCE droplet was deposited on the surface of a 2 mm-diameter silver/silver tetrakis-(pentafluorophenyl)borate (Ag/AgTPFB) electrode [10], which was inserted into a Teflon cell and 1.5 mL aqueous solution was added on the top of it to overlap the droplet, a water/DCE interface was thus formed. The voltammograms at this interface were obtained in a three-electrode configuration (Fig. 1a) with the DCE droplet-covered Ag/AgTPFB electrode as the working electrode (WE), a Ag/AgCl wire and a Pt wire positioned in the aqueous solution as the reference electrode (RE) and counter electrode (CE), respectively. The electrochemical cell is depicted as follows:

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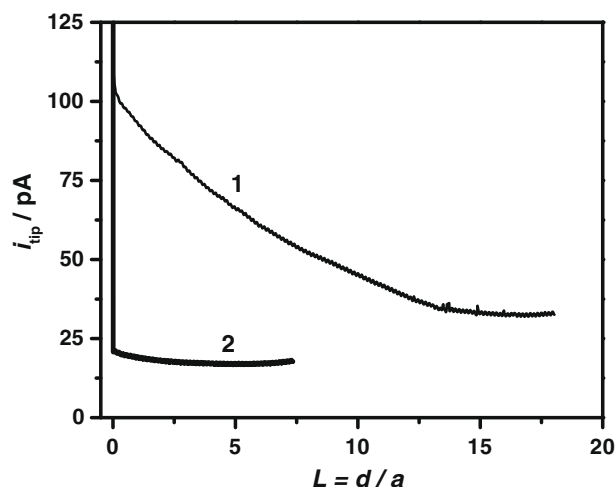


Fig. 3. Experimental approach curves with (Curve 1) and without (Curve 2) applying 0.45 V at the water/DCE interface: the tip potential 0.6 V and the approach rate $0.5 \mu\text{m s}^{-1}$.

water/DCE interface of 0.45 V. A gradual increase in the tip current due to the oxidation of H_2O_2 was observed as the tip approaches the water/DCE interface (Curve 1 in Fig. 3). The sharp increase of the tip current indicates a contact of the tip with the interface (due to oxidation of DMFc in DCE), which is taken as the zero tip-interface distance. Note that a control approach curve (Curve 2 in Fig. 3) was also measured by keeping the substrate Ag/AgTPFB electrode open circuited, in which no tip current increase was observed as no H_2O_2 was produced. Based on this feedback operation, the Pt microelectrode can be positioned about $15 \sim 20 \mu\text{m}$ above the water/DCE interface.

The final detection of H_2O_2 generated at the interface was based on the SG/TC operation mode in two ways. First, a LSV was measured at the tip when a constant potential of 0.45 V was applied at the water/DCE interface. As shown in Fig. 4a, instead of a conventional steady-state behavior at a microdisk electrode, a peak-shaped wave is observed at about 0.6 V, which is due to the H_2O_2 oxidation at the Pt microelectrode is not diffusion-controlled as it involves some surface reactions with platinum oxide [13,14].

Alternatively, the detection of H_2O_2 by SECM was performed using the method described by Zhou et al. [15], where the tip potential was held at 0.6 V and the Galvani potential difference across the water/DCE interface was cycled between -0.25 and 0.45 V. In this case, the cyclic voltammograms of the water/DCE interface and the tip current can be recorded simultaneously, as shown in Fig. 4b and c. The cyclic voltammogram of the water/DCE interface (Fig. 4b) is similar to the one observed in Fig. 2a with an irreversible current rising at positive potentials ($0.25\text{--}0.45$ V). Accordingly, in this potential range, the tip current on the forward scan (solid curve in Fig. 4c) for the oxidation of H_2O_2 increases as the Galvani potential difference becomes more positive (solid curve in Fig. 4b). When sweeping the Galvani potential difference across the water/DCE interface backward from 0.45 V to a lower value (dotted curve in Fig. 4b), the tip current (dotted curve in Fig. 4c) continues to increase and then falls following the decrease of the current at the water/DCE interface. At potentials below 0.25 V on the forward scan, the tip current is constant at a residual plateau value indicating that the production of H_2O_2 at the water/DCE interface does not occur. The synchronicity between the tip and interface current proves that the generation of H_2O_2 at the water/DCE interface is an interface potential-dependent process. The interface functions as a proton pump driven by the Galvani potential difference and the reaction pathway can be expressed as:

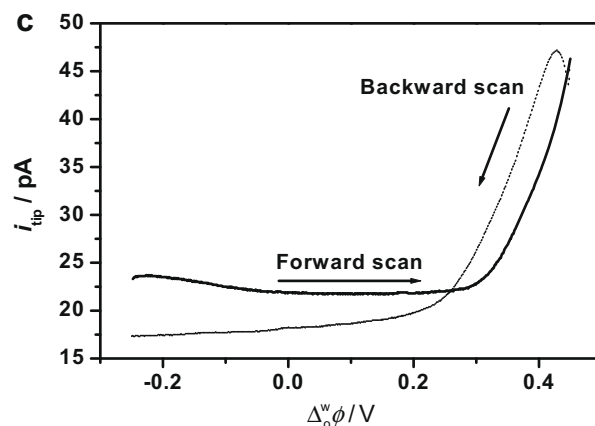
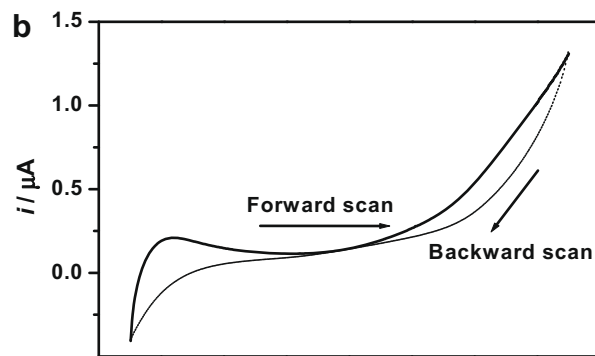
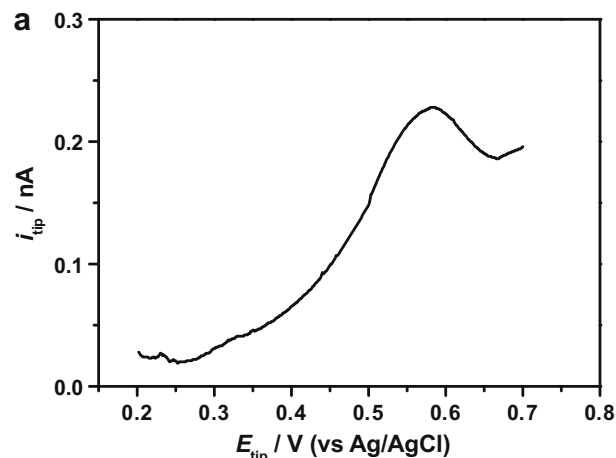
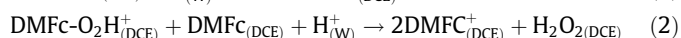
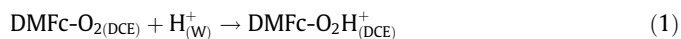


Fig. 4. (a) LSV at the Pt microelectrode obtained by applying 0.45 V at the water/DCE interface. The tip-interface distance $20 \mu\text{m}$ and the scan rate 10 mV s^{-1} , (b) Substrate and (c) tip voltammograms obtained with the tip potential held at 0.6 V and the Galvani potential difference across the water/DCE interface was scanned from -0.25 to 0.45 V at a scan rate of 10 mV s^{-1} . The tip-interface distance was $15 \mu\text{m}$.



Density functional theory (DFT) calculations (details not shown here) have shown that DMFc preferentially complexes with O_2 to form a superoxide adduct, which can further bind a proton from water. This protonated superoxide species can be reduced by a second DMFc to produce H_2O_2 . Considering that H_2O_2 is very hydrophilic, any H_2O_2 produced on the organic side of the interface is extracted to water [4], and can therefore be detected at the SECM tip.

4. Conclusions

The produced H_2O_2 at the water/DCE interface was successfully detected by SECM combined with a droplet method in a substrate generation/tip collection mode on the basis of monitoring the tip current. The resulting tip current for the H_2O_2 oxidation is concomitant with the substrate current due to the H_2O_2 production, which was found to be dependent on the Galvani potential difference across the water/DCE interface. Further work is required to unravel the kinetic aspects of this mechanism.

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